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Direct Flotation of Potash From Carnallite

By D. G. Foot, Jr., C. E. Jordan,
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UNITED STATES DEPARTMENT OF THE INTERIOR

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DIRECT FLOTATION OF POTASH FROM CARNALLITE

By D. G. Foot, Jr.,[1] C. E. Jordan,[2] and J. L. Huiatt[3]

ABSTRACT

The Bureau of Mines devised a direct flotation method for recovering potash from carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) ore characterized by a high content of water-insoluble impurities. The method includes (1) a decomposition leach of the carnallite, (2) flocculation-depression of the insoluble slimes, (3) potash rougher, cleaner, and recleaner flotation, and (4) final product leaching. The technique eliminates the necessity for removing the water-insoluble slimes by mechanical or flotation desliming. Laboratory results demonstrated that the direct flotation procedure, when compared with conventional techniques, yielded equivalent or improved flotation results with equal or less reagent consumption. Locked-cycle testing of the direct flotation method recovered 87.8 pct of the potassium in the flotation feed in a final product containing 60.6 pct K_2O. A flowsheet incorporating the carnallite leaching-potash flotation procedure is presented.

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INTRODUCTION

One objective of the Bureau of Mines mineral resources technology research program is to improve processing technology to enhance recovery, improve utilization, and reduce waste of minerals-based materials. To help achieve this objective, a research investigation was conducted to study a new, direct flotation method for the recovery of potash without prior removal of insoluble slimes.

The Permian Basin near Carlsbad, N. Mex., has been a source of high-grade sylvinite (a mixture of KCL and NaCl) ores during the last 40 years. As these high-grade sylvinite ores are depleted, low-grade sylvinite ore, containing abundant insoluble slimes, and carnallite ores are becoming the future sources for potash production. These ores contain 1 to 8 pct water-insoluble slimes, which must be removed prior to potash flotation because of their high absorptive capacity for the amine collectors used in potash flotation. Insoluble slimes conventionally are removed by scrubbing the ore, followed by hydroclassification to separate the slimes from the coarse ore, as reported by Atwood (1)[4] and Browning (3). Residual insoluble slimes not removed by hydroclassification are blinded with reagents such as guar gum or starch to prevent interference in subsequent potash flotation.

Another method gaining in commercial usage is insoluble slimes flotation prior to potash flotation (2, 4-7). In these processes, slimes are flocculated and then floated with a variety of reagents. Losses of potash to the slimes product are generally less than those achieved by mechanical desliming.

With the significant potash losses in the discarded insoluble slimes and the difficulty in removing insoluble slimes, improved methods are needed that will minimize these problems. In this regard, a direct flotation method has been investigated as an alternative to mechanical desliming and flotation desliming.

EXPERIMENTAL MATERIALS

A carnallite ore containing high amounts of water insolubles from the Carlsbad, N. Mex., area was used in this study. Chemical analysis of the ore is shown in table 1.

TABLE 1. - Chemical analysis of carnallite ore, wt-pct

K_2O	11.8
Sodium	17.0
Magnesium	4.0
Calcium	.2
Sulfate	2.5
Chloride	46.0
Water insolubles	4.0

Petrographic and X-ray diffraction analyses of the carnallite ore indicated that it contained, in weight-percent, 43 carnallite, 7 sylvite (KCl), 43 halite (NaCl), and 4 water-insoluble slimes. Some carnallite and sylvite contained minor amounts of occluded hematite (Fe_2O_3), which gave the minerals a distinct red color. Minor amounts of polyhalite ($MgSO_4 \cdot K_2SO_4 \cdot 2CaSO_4 \cdot 2H_2O$), kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) and leonite ($MgSO_4 \cdot K_2SO_4 \cdot 4H_2O$) were also present. The water-insoluble fraction of the ore was all minus 150 mesh and contained abundant magnesite, chlorite, and illite. The liberation size of the sylvite and the original carnallite was 10 mesh.

Minus 4-inch carnallite ore was prepared for bench-scale flotation testing

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

by stage crushing in a jaw and roll crusher through 10 mesh. Screen analysis of the ore, shown in table 2, indicated that only 18 pct of the final crushed weight was finer than 100 mesh.

TABLE 2. - Screen analysis of carnallite ore

Screen size, mesh:	Wt-pct
Plus 10	-
Minus 10 plus 14	17.6
Minus 14 plus 20	21.2
Minus 20 plus 28	12.8
Minus 28 plus 35	11.7
Minus 35 plus 48	8.2
Minus 48 plus 65	4.7
Minus 65 plus 100	5.8
Minus 100	18.0

Reagents used in this study were all commercially available. They include (1) an emulsion of Armeen TD[5] (a primary alphatic tallow amine) neutralized with HCl and Barrett's 634 flotation oil in tapwater, (2) MRL-201 guar gum insoluble slimes blinder, (3) an insoluble slimes flocculant, Superfloc-127 (a high-molecular-weight, nonionic polyacrylamide), and (4) the insoluble slimes flotation collector, Aeropromotor 870 (a cationic surfactant which is a mixture of octadecyl amine and octadecyl guanidine salts of octadecyl carbamic acid reacted with ethylene oxide). Hexanol frother was used as needed in all tests. All reagent consumptions are expressed as pounds of reagent per short ton of ore (lb/ton).

Other slime blinders such as starch, dextrin, and carboxymethylcellulose were investigated and found to be less effective than the guar gum. Various amines were studied as potash collectors; Armeen TD was found to be most selective. A 1:1 ratio of Armeen TD to Barrett's oil was found to produce the best suited emulsion for potash flotation. This trend was evident in each of the flotation methods evaluated.

An equilibrium brine containing, in weight-percent, 1.9 K_2O, 0.8 Na, and 6.5 Mg was used for the carnallite flotation work. The density of the brine was 1.278 grams per cubic centimeter.

EXPERIMENTAL PROCEDURES AND RESULTS

Decomposition Leaching the Carnallite Ore

Because direct flotation of the carnallite yielded only about 60-pct potassium recovery at a grade of 39 pct K_2O, it was necessary to decompose the carnallite to KCl to produce a feed material for efficient potash flotation. Various decomposition-leach procedures were tested on a laboratory scale, which led to the adoption of the following standard procedure. The carnallite ore was diluted to 60-pct solids pulp density in equilibrium brine, and the slurry was agitated at a 720-ft/min peripheral impeller speed. Fresh water was added to dissolve the $MgCl_2$, leaving a solid KCl product. Approximately 400 pounds of

[5]Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

fresh water per ton of 43-pct-carnallite ore was added to the slurry all at once, followed by flotation reagent conditioning. If less water was added, incomplete carnallite decomposition occurred, reducing the final product grade. This procedure was selected because of the short retention time and completeness of the carnallite conversion. The feed particle size of minus 10 mesh was not altered by the decomposition leach.

A major concern was the amount of potassium dissolved in the brine during the decomposition leach. Laboratory tests were conducted in which the decomposition-leach time was varied up to 3.0 hours by stage addition of the water. Potassium dissolution varied slightly, showing little dependency on leach time. The standard procedure adopted, which added the water all at once, showed only 10.5-pct potassium dissolution in the brine. Changes in brine composition were minimal on batch-scale tests.

Two-Stage Mechanical Desliming

Following decomposition leaching, 2.2-pound samples of the carnallite ore were scrubbed with saturated equilibrium brine at a pulp density of 27 pct solids

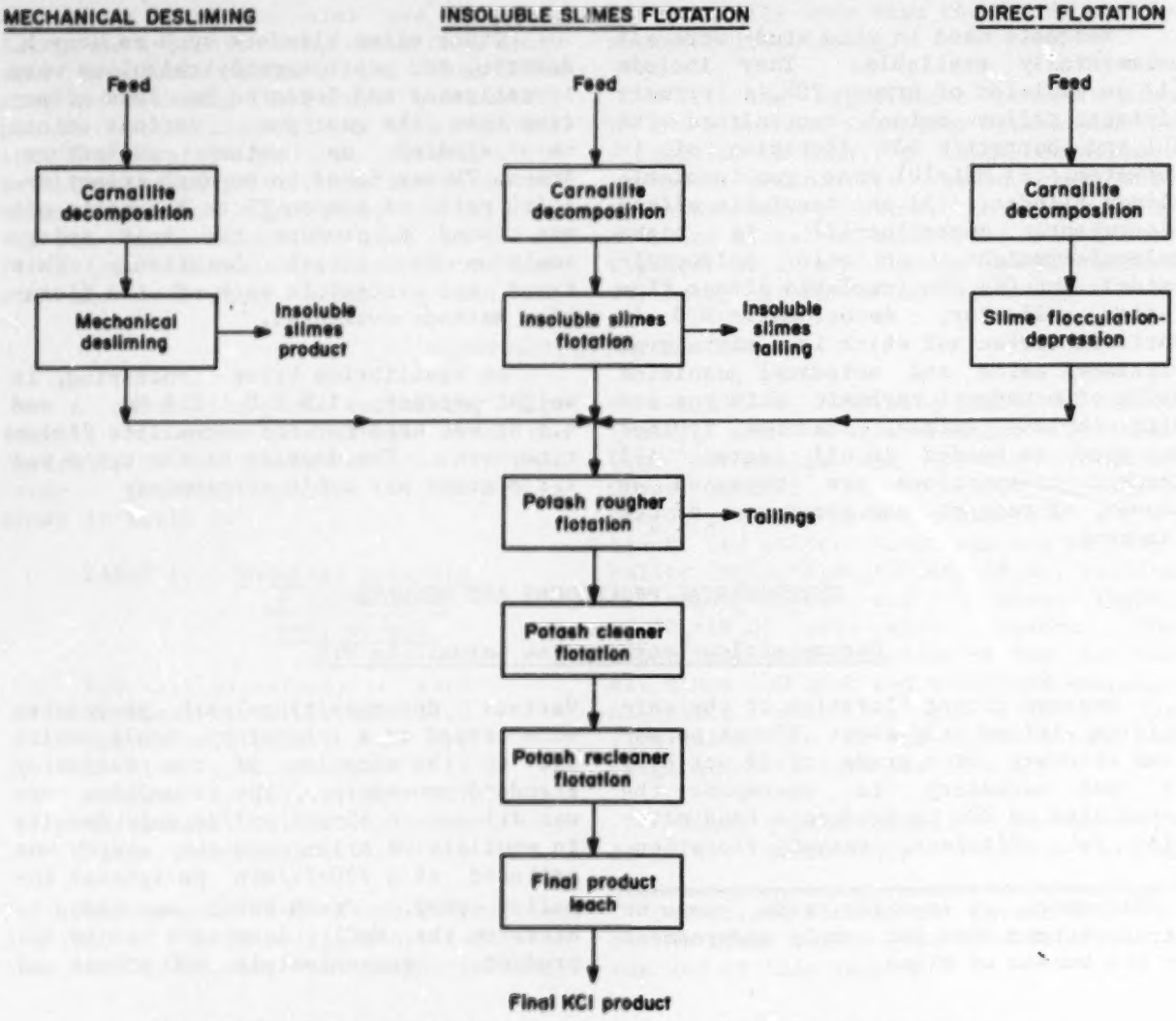

FIGURE 1. - Flowsheet for bench-scale flotation of potash from carnallite ore.

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for 15 minutes in a Fagergren laboratory flotation cell using an 830-ft/min peripheral impeller speed. The slurry was decanted onto a vibrating 150-mesh screen (as used in commercial operations) to separate the tailings. The final deslimed material, screen oversize, was used as potash flotation feed. A flowsheet of the mechanical desliming procedure along with those of insoluble slimes flotation and insoluble slimes depression derived from batch testing is illustrated in figure 1. Note that the subsequent potash recovery scheme is identical for all three individual insoluble slimes treatment methods.

Flotation of the deslimed pulp was performed at 23-pct-solids pulp density. The pulp was conditioned for 2 min with 0.2 lb/ton MRL-201 insoluble slimes blinder and for an additional 2 min with 0.2 lb/ton amine-Barrett's oil emulsion.

After conditioning, a drop of hexanol corresponding to 0.02 lb/ton was added, and a potash flotation rougher concentrate was collected for 1.5 min at a peripheral impeller speed of 930 ft/min. This procedure was repeated three times. Total reagent additions were 0.8 lb/ton MRL-201 insoluble slimes blinder, 0.8 lb/ton amine-Barrett's oil emulsion, and 0.08 lb/ton hexanol. The long residence time required for flotation of the carnallite-bearing ore was attributed to the viscosity of the high-magnesium brine, which can slow flotation response. The potash rougher concentrates were combined in a 500-gram Galigher Model LA 500 flotation cell for cleaner flotation. The combined pulp was agitated for 1 min without additional reagents. Air was introduced, and a cleaner product was collected for 2 minutes. The cleaner concentrate was replaced in the 500-gram Galigher flotation cell, and a recleaner product then was collected for 2 min without additional reagents.

The optimum results obtained using mechanical desliming are shown in table 3. About 71 pct of the potassium in the flotation feed was recovered in the final KCl product at a grade of 60.2 pct K_2O, and 18 pct was lost in the slimes. The potash recovery represents feed to flotation and does not take into account the 10.5 pct potash lost to the brine during the decomposition leach stage.

TABLE 3. - Product analyses and distribution for mechanical desliming

Product	Wt-pct	Analyses, wt-pct		Distribution, pct	
		K_2O	Water insolubles	K_2O	Water insolubles
Final KCl product[1]...	12.9	60.2	0.9	71.3	2.9
Recleaner tailings...	8.2	5.6	1.2	4.3	2.5
Cleaner tailings.....	7.9	4.3	3.2	3.2	6.4
Salt tailings.....	49.9	.7	1.2	3.2	15.2
Slimes tailings.....	21.2	9.2	13.6	18.0	73.0

[1]Includes water leach of final product.

The final KCl product produced by each method described contained small amounts of NaCl which had to be removed to produce a marketable potash product. These products were subjected to a spray water leach at an optimum solid-to-water ratio of 4:1. This method removed the fine NaCl while limiting potash losses to less than 0.5 wt-pct of the final product. Because the leach water was added during filtration, retention time was short, which kept potassium dissolution below the theoretical value.

The disadvantages of mechanical desliming are (1) high potash losses to

the deslimed products, (2) higher brine requirements due to the excess brine required to mechanically deslime the ore, and (3) the necessity of slimes treatment, which means an additional operating step.

Insoluble Slimes Flotation

Batch insoluble slimes flotation tests were conducted in a Fagergren laboratory flotation cell. In each test, following the decomposition leach, 2.2 pounds of ore was scrubbed for 5 min at a pulp density of 27-pct-solids in a saturated brine at an 830-ft/min peripheral impeller speed to disperse the insoluble slimes. The impeller speed was reduced to 720 ft/min, flocculant and collector were added, air was introduced immediately, and an insoluble slimes froth product was collected for 2 min. The optimum flocculant and collector additions are shown in table 4. The flotation procedure was repeated once. All tests were performed at a natural brine pH of 7.0 with total flotation time of 2 to 4 min. A flowsheet for this procedure is also shown in figure 1. The subsequent potash flotation procedure was the same as that used in mechanical desliming tests. Blinder and collector additions used in the potash flotation step are also shown in table 4.

TABLE 4. - Total reagent additions for insoluble slimes flotation

	Addition, lb/ton
Superfloc-127	0.2
Aeropromoter 870	.4
MRL-201	.8
Amine-Barrett's oil (1:1)	.8

Results obtained in insoluble slimes flotation tests are shown in table 5. Final KCl product recoveries were higher than those achieved using mechanical desliming owing to decreased potash loss to the tailings.

TABLE 5. - Product analyses and distribution for insoluble slimes flotation

Product	Wt-pct	Analyses, wt-pct		Distribution,[1] pct	
		K_2O	Water insolubles	K_2O	Water insolubles
Final KCl product	14.7	60.3	0.9	82.3	3.3
Recleaner tailings	7.1	4.2	2.0	2.7	3.6
Cleaner tailings	8.2	1.8	3.0	1.4	6.1
Salt tailings	66.0	.7	1.7	4.3	28.0
Insoluble slimes tailings	4.0	25.0	59.0	9.3	59.0

[1] K_2O distribution does not take into consideration the 10.5-pct loss during decomposition of the carnallite.

Direct Potash Flotation

In a third procedure tested, carnallite ore was diluted to 23-pct-solids pulp density in a Fagergren laboratory flotation cell after a decomposition leach. The pulp was conditioned at an 830-ft/min peripheral impeller speed for 2 min, first with Superfloc-127, a high-molecular-weight, nonionic flocculant, and then with MRL-201 insoluble slimes blinder. The pulp was then conditioned an additional 2 minutes with amine and flotation oil. Air was introduced, and a potash rougher concentrate was collected for 2 min. This procedure was repeated three times. The potash rougher concentrate was then cleaned and recleaned, with no reagents added, to produce the final potash product. A final product leach was used to bring the product to a marketable grade. The simplified flowsheet is shown in figure 1.

Results of optimization testing of the amount of MRL-201 insoluble slimes blinder showed optimum slime depression in conjunction with subsequent potash removal at a total reagent addition of 1.2 lb/ton. These results are shown in figure 2 with addition of MRL-201 in excess of 1.2 lb/ton, the insoluble slimes continued to blind; however, the MRL-201 had a depressing effect upon the

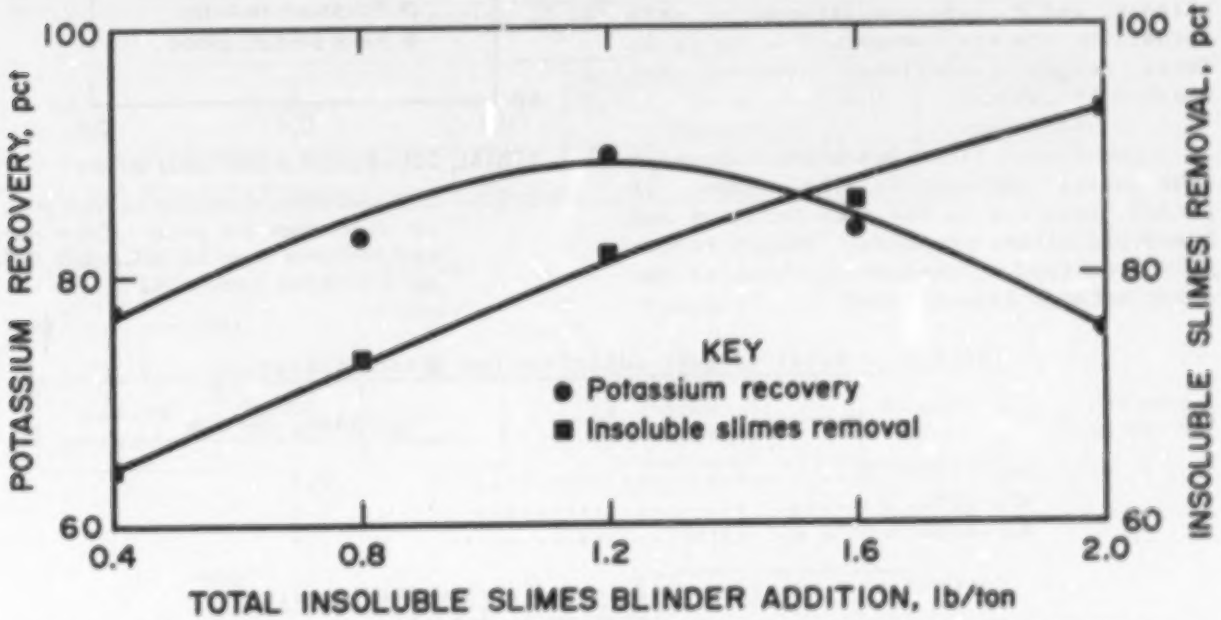

FIGURE 2. - Effect of insoluble slimes blinder on insoluble slimes removal and potassium recovery during rougher flotation. (Other reagent additions were 0.2 lb/ton Superfloc-127 and 0.4 lb/ton amine per barrel of oil.)

sylvite, thereby reducing the potassium recovery.

Optimization of the potash collector additions (fig. 3) showed that best results were achieved using a 0.4-lb/ton addition. Lesser amounts recovered less potassium, while greater amounts reduced the final product grade owing to promotion of the halite.

Flocculant was added to the point of complete insoluble slimes flocculation, 0.3 lb/ton, with additional reagent addition showing no effect on potash recoveries or grades.

Test results for optimum flocculant, blinder, and collector additions for this carnallite ore are summarized in table 6. These reagent additions produced the results in table 7.

The direct flotation method showed a substantial decrease in the amount of potash discarded in the salt tailings and insoluble slimes products. Potash recoveries remained equivalent to those of the other methods investigated.

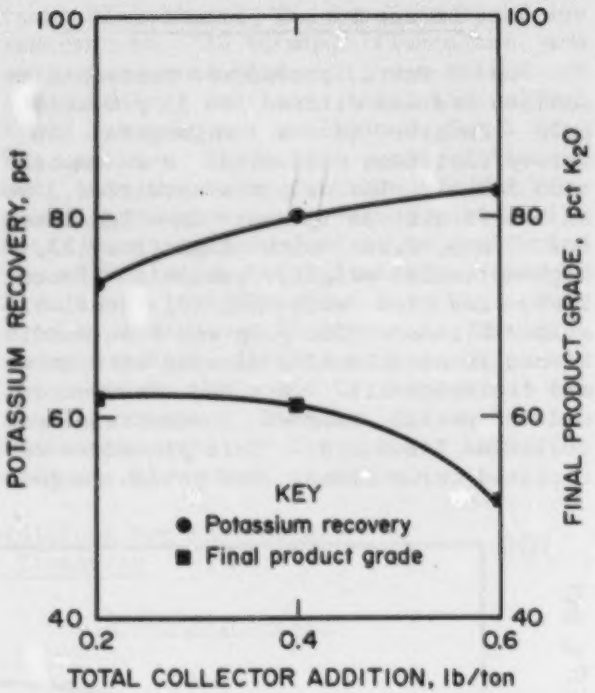

FIGURE 3. - Effect of collector addition on final product concentrate and grade. (Other reagent additions were 1.2 lb/ton MRL-201 and 0.15 lb/ton Superfloc-127.)

TABLE 6. - Total reagent additions for direct flotation

	Addition, lb/ton
Superfloc-127	0.3
MRL-201	1.2
Amine-Barrett's oil (1:1)	.4

TABLE 7. - Product analyses and distribution for direct flotation of potash

Product	Wt-pct	Analyses, wt-pct		Distribution,[1] pct	
		K_2O	Water insolubles	K_2O	Water insolubles
Final KCl product	14.5	60.5	0.6	81.6	2.4
Recleaner tailings	4.3	11.6	2.3	4.6	2.8
Cleaner tailings	8.4	5.5	5.1	4.3	11.9
Tailings[2]	72.8	1.4	4.1	9.5	82.9

[1] K_2O distribution does not take into consideration the 10.5-pct loss during decomposition of the carnallite.

[2] Salt plus insoluble slimes.

Locked-Cycle Flotation Testing

Locked-cycle flotation testing was performed to determine the effect of the presence of middling products and brine recycle on insoluble slimes depression and subsequent potash flotation, and to obtain data for process scale-up. The cleaner and recleaner tailings were classified at 150 mesh with the coarse product returning to the head of the rougher and cleaner circuits respectively. The flowsheet is shown in figure 4. Undersize material for both classification steps was discarded in the tailings.

Four complete cycles were made to insure that the circuit was at equilibrium. Metallurgical results are shown in table 8. Nearly 88 pct of the potassium was recovered in the final KCl product at a grade of 60.6 pct K_2O. The final tailings, a combined product containing the undersize material from the classification of the recleaner and cleaner flotation stages as well as the salt-insoluble slimes tailings, contained 98.7 pct of the insoluble slimes. Recycling the products and the brine gave slightly improved results over those obtained by batch flotation.

TABLE 8. - Product analyses and distribution for locked-cycle testing of the direct flotation method

Product	Wt-pct	Analyses, wt-pct		Distribution, pct	
		K_2O	Water insolubles	K_2O	Water insolubles
Final KCl product....	15.9	60.6	0.3	87.8	1.3
Final tailings.....	84.1	1.6	4.7	12.2	98.7

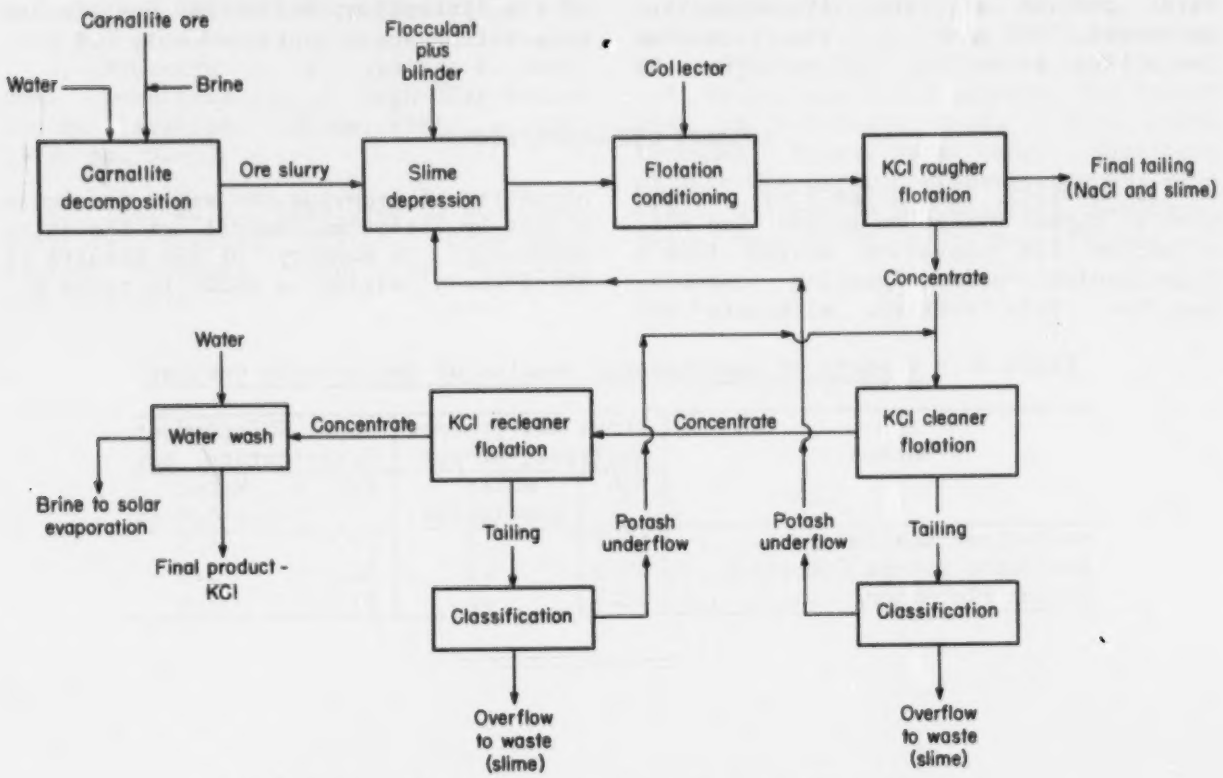

FIGURE 4. - Flowsheet for the direct flotation of carnallite ore.

During locked-cycle testing, brine was recycled as completely as possible. Other laboratory testing determined that an excess brine balance occurred at times. The excess brine came from the water added during the decomposition leach and the water released from the carnallite crystal. During decomposition 56 gal of additional brine per ton of ore was generated. The actual amount of excess brine realized would depend on the efficiency of debrining the products. Solar evaporation studies performed to recover the potassium from the excess brine showed that over 96 pct of the potassium in the brine was recovered in an evaporite that contained, in weight-percent, 60 carnallite, 10 sylvite, and 30 halite. The procedure used to recover the potash from the evaporite was the same as the direct flotation method except that no insoluble slimes depression was necessary because there were no slimes present. Flotation of the sylvite, after decomposition leach of the carnallite using 520 pounds of fresh water per ton of carnallite evaporite, recovered 95.8 pct of the potassium in a final product of 60.1 pct K_2O. By evaporation and flotation of the potash in the excess plant brine, the overall potassium dissolution to the brine was reduced to less than 3 pct. The optimum collector addition was 0.2 lb/ton.

In a commercial operation, the evaporite would be blended with the run-of-mine carnallite ore instead of being treated separately. Bench-scale testing on blended ore containing 5, 10, and 15 pct evaporite was performed using the direct flotation method at the optimum reagent additions shown in table 6. Very little variance in recoveries, 79.8, 80.1, and 82.1 pct, or final product grades, 60.1, 60.9, and 60.3 pct K_2O, was observed.

When products were mathematically combined for the direct flotation method, taking into account locked-cycle and solar evaporation-flotation results, 87.8 pct of the potassium in the ore reported to a final product of 60.0 pct K_2O. Final tailings contained 11.6 pct of the potassium, while the waste solar evaporation brine contained only 0.6 pct.

SUMMARY AND CONCLUSIONS

Laboratory investigations showed that a direct flotation method was most effective for recovering potash from a high-insoluble-slime bearing carnallite ore. This technique eliminated the necessity of removing the water-insoluble slimes by either mechanical or flotation desliming. A summary of the results of batch-scale testing is shown in table 9.

TABLE 9. - Summary of experimental results of batch-scale testing

Method	Final KCl product analyses, wt-pct		Final KCl product distribution, pct	
	K_2O	Water insolubles	K_2O	Water insolubles
Mechanical desliming.....	60.2	0.9	71.3	2.9
Insoluble slimes flotation...	60.3	.9	82.3	3.3
Direct flotation.....	60.5	.6	81.6	2.4

Locked-cycle testing of the direct flotation method recovered 87.8 pct of the solid-phase KCl and a final product at a grade of 60.6 pct K_2O.

In comparative tests with conventional techniques, advantages of the direct flotation methods are (1) insoluble slimes removal is not necessary prior to flotation of the potash, (2) the detrimental effect of the presence of insoluble slimes on potash flotation is minimized, (3) equivalent or improved removal of insoluble slimes can be achieved, (4) reagent additions are equivalent or lower, and (5) potassium losses to the discarded insoluble slimes are reduced.

Based on the data derived from bench-scale investigations of the direct flotation method presented in this report, a continuous 100-lb/hr process investigation unit is being operated to further evaluate the direct flotation method.

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